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Title: JP10172615A2: NONAQUEOUS SOLVENT BATTERY AND POLYME
ELECTROLYTE SECONDARY BATTERY

Country: JP Japan

Kind: A

Inventor: ARAI YOSHIYO;
KATSUMATA TOMOO;

Assignee: TOSHIBA BATTERY CO LTD
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Published / Filed: 1998-06-26 / 1996-12-17

Application JP1996000336854

Number:

IPC Code: [H01M 10/40](#); [H01M 2/16](#); [H01M 4/02](#); [H01M 4/62](#);

Priority Number: 1996-12-17 JP1996000336854

Abstract:


... PROBLEM TO BE SOLVED: To provide a polymer electrolyte secondary battery in which burning hazard is avoided when a battery inside temperature becomes abnormally high resulting from overcharge or the like, and safety is enhanced.

... SOLUTION: A polymer electrolyte secondary battery is provided with a positive electrode 2 which contains active material, nonaqueous electrolyte, and a polymer holding the electrolyte, a negative electrode 4 which contains active material storing and discharging lithium ions, nonaqueous electrolyte, a polymer holding the electrolyte, a solid polymer electrolyte layer 5 which is arranged between the positive electrode and the negative electrode, and contains nonaqueous electrolyte, and a polymer holding the electrolyte. At least one among the positive electrode, the negative electrode, and the solid polymer electrolyte layer contains a flame retardant producing a volatile nonflammable substance at a high temperature.

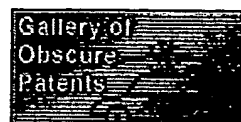
... COPYRIGHT: (C)1998,JPO

Family: None

Forward
References:

PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6168885	2001-01-02	Narang; Subhash C.	SRI International	Fabrication of electrodes a devices containing electro

Other Abstract CHEMABS 129(05)056517Y CAN129(05)056517Y DERABS C98-419423 DERC98-41
Info:



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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-172615

(43) 公開日 平成10年(1998)6月26日

(51) Int. Cl.⁴

H01M 10/40

識別記号

2/16

4/02

4/62

P I

H01M 10/40

Z

B

2/16

4/02

4/62

Z

D

Z

審査請求 未請求 請求項の数 3 O L (全 8 頁)

(21) 出願番号

特願平8-336354

(22) 出願日

平成8年(1996)12月17日

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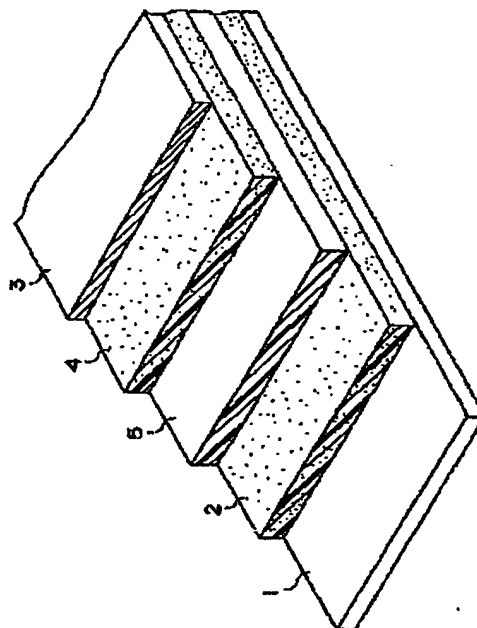
(74) 代理人 弁理士 鈴江 武彦 (外6名)

(54) 【発明の名称】 非水電解液電池及びポリマー電解質二次電池

(57) 【要約】

【課題】 過充電等により電池内の温度が異常高温になった際の燃焼の危険が回避され、安全性が向上されたポリマー電解質二次電池を提供することを目的とする。

【解決手段】 活物質、非水電解液及びこの電解液を保持するポリマーを含む正極と、リチウムイオンを吸蔵・放出する活物質、非水電解液及びこの電解液を保持するポリマーを含む負極と、前記正極及び前記負極の間に配置され、かつ非水電解液及びこの電解液を保持するポリマーを含む固体ポリマー電解質層5とを具備し、前記正極、前記負極及び前記固体ポリマー電解質層のうち少なくとも一つは、高温において担持性の不燃性物質を生成する難燃剤を含むことを特徴とするポリマー電解質二次電池である。



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【特許請求の範囲】

【請求項1】 正極と、負極と、非水電解液と、前記正極と前記負極を絶縁し、かつ前記電解液を保持する機能を有するセパレータとを具備し、前記正極、前記負極及び前記セパレータのうち少なくとも一つは、高温において揮発性の不燃性物質を生成する難燃剤を含むことを特徴とする非水溶媒電池。

【請求項2】 活物質、非水電解液及びこの電解液を保持するポリマーを含む正極と、リチウムイオンを吸蔵・放出する活物質、非水電解液及びこの電解液を保持するポリマーを含む負極と、前記正極及び前記負極の間に配置され、かつ非水電解液及びこの電解液を保持するポリマーを含む固体ポリマー電解質層とを具備し、前記正極、前記負極及び前記固体ポリマー電解質層のうち少なくとも一つは、高温において揮発性の不燃性物質を生成する難燃剤を含むことを特徴とするポリマー電解質二次電池。

【請求項3】 前記難燃剤は、テトラプロモビスフェノールAからなるか、もしくはテトラプロモビスフェノールAと酸化アンチモンからなることを特徴とする請求項2記載のポリマー電解質二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、非水電解液を備える非水溶媒電池及びポリマー電解質二次電池に係わる。

【0002】

【従来の技術】 近年、電子機器の発達に伴い、小型で軽微、かつエネルギー密度が高く、更に繰り返し充放電が可能な二次電池の開発が要望されている。このような二次電池としては、リチウム又はリチウム合金を活物質とする負極と、モリブデン、バナジウム、チタンあるいはニオブ等の酸化物、硫化物もしくはセレン化合物を活物質とする正極とを具備したリチウム二次電池が知られている。

【0003】 しかしながら、リチウム又はリチウム合金を活物質とする負極を備えた二次電池は、充放電サイクルを繰り返すと負極にリチウムのデンドライトが発生するため、充放電サイクル寿命が短いという問題点がある。

【0004】 このようなことから、負極に、例えばコークス、黒鉛、炭素繊維、樹脂焼成体、熱分解気相炭素のようなリチウムイオンを吸蔵・放出する炭素質材料を用いたリチウム二次電池が提案されている。前記リチウムイオン二次電池は、デンドライト析出による負極特性の劣化を改善することができると、電池寿命と安全性を向上することができる。

【0005】 リチウムイオン二次電池の一例であるポリマー電解質二次電池として、米国特許公報第5, 29 6, 318号に正極、負極及び電解質層にポリマーを添加することにより柔軟性が付与されたハイブリッド高

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子電解質を有する再充電可能なリチウムインターカレーション電池が開示されている。このポリマー電解質二次電池は、活物質、非水電解液及びこの電解液を保持するポリマーを含む正極層が集電体に担持された構造の正極と、リチウムイオンを吸蔵・放出する炭素質材料、非水電解液及びこの電解液を保持するポリマーを含む負極層が集電体に担持された構造の負極と、前記正極層及び前記負極層の間に介在され、かつ非水電解液及びこの電解液を保持するポリマーを含む固体ポリマー電解質層とを有するものである。前記非水電解液としては、非水溶媒にリチウム塩を溶解したものが用いられている。この非水溶媒には、通常、引火性の有機溶媒が用いられる。従って、前記二次電池は、過充電や、あるいは近くに火気が存在する等により電池内の温度が上昇し、異常高温になると、前記非水溶媒が発火する恐れがあるため、これに対する安全性の確保が重要な課題となる。

【0006】 ところで、前記正極、前記負極及び前記固体ポリマー電解質層にそれぞれ含まれる非水電解液を保持するポリマーとしては、従来、フッ化ビニリデン(VdF)-ヘキサフルオロプロピレン(HFP)の共重合体が用いられている。この共重合体において、VdFは共重合体の骨格部で機械強度の向上に寄与し、また非水電解液を保持する。HFPは共重合体に非晶質の状態で取り込まれ、リチウムイオンの透過部として機能し、またVdFにおける非水電解液の保持に寄与する。このVdF-HFP共重合体は、ハロゲン元素を含むために、自己消火性を有する。例えば、VdF-HFP共重合体をフィルム状に加工した後、これに火元を近づけると、炎が燃え移ってフィルムが燃焼するが、火元をフィルムから遠ざけるとフィルムの燃焼が止む。しかしながら、このようなポリマー電解質二次電池においては、さらなる安全性の向上が要望されている。

【0007】

【発明が解決しようとする課題】 本発明の目的は、過充電等により電池内の温度が異常高温になった際の燃焼の危険が回避され、安全性が向上された非水溶媒電池及びポリマー電解質二次電池を提供しようとするものである。

【0008】

【課題を解決するための手段】 本発明に係わる非水溶媒電池は、正極と、負極と、非水電解液と、前記正極と前記負極を絶縁し、かつ前記電解液を保持する機能を有するセパレータとを具備し、前記正極、前記負極及び前記セパレータのうち少なくとも一つは、高温において揮発性の不燃性物質を生成する難燃剤を含むことを特徴とするものである。

【0009】 本発明に係わるポリマー電解質二次電池は、活物質、非水電解液及びこの電解液を保持するポリマーを含む正極と、リチウムイオンを吸蔵・放出する活物質、非水電解液及びこの電解液を保持するポリマーを

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モリブデンなど)等を挙げることができる。中でも、リチウムマンガン複合酸化物、リチウム含有コバルト酸化物、リチウム含有ニッケル酸化物を用いるのが好ましい。

【0028】前記非水電解液を保持するポリマーとしては、前述したポリマー電解質層で説明したのと同様なものを挙げることができる。前記正極の前記正極層に例えば人造黒鉛、カーボンブラック（例えばアセチレンブラックなど）、ニッケル粉末等の導電性材料を添加してもよい。

【0029】前記集電体としては、アルミニウム箔、アルミニウムメッシュ、アルミニウム製エキスパンドメタル、アルミニウム製パンチドメタル等を挙げることができ、

【0030】前記正極は、例えば以下に説明する(1)～(2)の方法によって作製することができる。

(1) 非水電解液を保持するポリマーの溶液を調製し、この溶液に前記燃焼剤、前記活性物質及び前記導電材料を添加した後、これらを混合し、成膜することにより正極

層を作製する。この正極層と前記集電体とを例えば熱圧着等によって接着する。前記正極層に非水電解液を含浸させることにより正極を作製する。

【0031】(2) 非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記凝集剤、前記活性物質及び前記導電材料を添加した後、これらを混合し、正極用ペーストを調製する。この正極用ペーストを前記集電体に塗工した後、乾燥させる。前記正極層に非水電解液を含浸させ、正極を作製する。

【0032】＜正極B＞前記正極Bは、活物質、非水電解液およびこの電解液を保持するポリマーを含む正極層が集電体に担持された構造を有する。

【0033】前記活物質、非水電解液、ポリマー及び集電体としては、前述した正極Aで説明したのと同様なものが用いられる。前記正極は、例えば以下に説明する(1)～(2)の方法によって作製することができ、

【0034】(1) 非水電解液を保持するポリマーの溶液を調製し、この溶液に前記活動物質及び前記導電材料を添加した後、これらを混合し、成膜することにより正極層を作製する。この正極層と前記集電体を例えば熱圧着等によって接合する。前記正極層に非水電解液を含浸させることにより正極を作製する。

【0035】(2) 非水電解液を保持するポリマーの溶液を調製し、前記溶液に前記活性物質及び前記導電材料を添加した後、これらを混合し、正極用ペーストを調製する。この正極用ペーストを前記集電体に塗工した後、乾燥させる。前記正極層に非水電解液を含浸させ、正極を作製する。

前記負極としては、以下に説明する負極Aか、または負極Bを用いることができる。

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【0037】＜負極A＞この負極Aは、リチウムイオンを吸蔵・放出する活物質、高温において揮発性の不燃性物質を生成する難燃剤、非水電解液及びこの電解液を保持するポリマーを含む負極層が集電体に担持された構造を有する。

【0038】前記難燃剤としては、前述したポリマー電解質層で説明したのと同様なものを用いることができる。前記難燃剤の配合量は、前記非水電解液を保持するポリマーに対して5～20重量%の範囲にすることが好ましい。これは次のような理由によるものである。前記配合量を5重量%未満にすると、難燃作用を十分に発揮することが困難になる恐れがある。一方、前記配合量が20重量%を超えると、負極層の機械的強度が極端に低下して電池の形状保持に影響を及ぼす恐れがある。より好ましい配合量は、8～15重量%の範囲である。

【0039】前記活物質としては、リチウムイオンを吸蔵・放出する炭素質材料を挙げることができる。かかる炭素質材料としては、例えば、有機高分子化合物（例えば、フェノール樹脂、ポリアクリロニトリル、セルロース等）を焼成することにより得られるもの、コークスや、ピッチを焼成することにより得られるもの、人造グラファイト、天然グラファイト等に代表される炭素質材料を挙げることができる。中でも、アルゴンガス、窒素ガス等の不活性ガス雰囲気中において、500℃～3000℃の温度で、常圧または減圧下にて前記有機高分子化合物を焼成して得られる炭素質材料を用いるのが好ましい。

【0040】前記非水電解液を保持するポリマーとしては、前述したポリマー電解質層で説明したのと同様なものを用いることができる。前記負極の前記負極層に入造グラファイト、天然グラファイト、カーボンブラック、アセチレンブラック、ケッチェンブラック、ニッケル粉末、ポリフェニレン誘導体等の導電性材料、オレフィン系ポリマーや炭素繊維等のフィラーを添加しても良い。

【0041】前記集電体としては、銅箔、銅メッシュ、銅製エキスパンドメタル、銅製パンチドメタル等を挙げることができる。前記負極Aは、例えば、以下に説明する（1）～（2）の方法によって作製することができる。

【0042】（1）非水電解液を保持するポリマーの溶液を調製し、この溶液に前記難燃剤及び前記活物質を添加した後、これらを混合し、成膜することにより負極層を作製した後、前記負極層と前記集電体とを例えば熱圧着等によって接合する。前記負極層に非水電解液を含浸させることにより負極を作製する。

【0043】（2）非水電解液を保持するポリマーの溶液を調製し、この溶液に前記難燃剤及び前記活物質を添加した後、これらを混合し、負極用ペーストを調製する。この負極用ペーストを前記集電体に塗工した後、乾燥させる。前記負極層に非水電解液を含浸させることに

より負極を作製する。

【0044】＜負極B＞この負極Bは、リチウムイオンを吸蔵・放出する活物質、非水電解液及びこの電解液を保持するポリマーを含む負極層が集電体に担持された構造を有する。

【0045】前記活物質、前記電解液、前記ポリマー及び前記集電体としては、前述した負極Aで説明したのと同様なものを挙げるることができる。前記負極Bは、例えば、以下に説明する（1）～（2）の方法によって作製することができる。

【0046】（1）非水電解液を保持するポリマーの溶液を調製し、この溶液に前記活物質を添加した後、これらを混合し、成膜することにより負極層を作製した後、前記負極層と前記集電体とを例えば熱圧着等によって接合する。前記負極層に非水電解液を含浸させることにより負極を作製する。

【0047】（2）非水電解液を保持するポリマーの溶液を調製し、この溶液に前記活物質を添加した後、これらを混合し、負極用ペーストを調製する。この負極用ペーストを前記集電体に塗工した後、乾燥させる。前記負極層に非水電解液を含浸させることにより負極を作製する。

【0048】なお、電解液未含浸の正極、電解液未含浸の電解質層および電解液未含浸の負極への電解液の含浸は、前述した図1に示す積層構造を対象にして一括して行ってもよい。

【0049】以上説明した本発明に係るポリマー電解質二次電池は、正極、負極及び固体ポリマー電解質層のうちいずれか一つの部材が高温において揮発性の不燃性物質を生成する難燃剤を含む。このような二次電池は、例えば過充電や、高温雰囲気中に晒されることによって電池内の温度が上昇すると、前記難燃剤が揮発性の不燃性物質を生成する。この不燃性物質は担持して不燃性ガスを発生する。このガス発生反応は、吸熱反応であるため、電池内の温度を低下させることができる。その結果、非水電解液が発火するのを未然に防ぐことができ、仮に非水電解液が既に燃焼していたとしても前記不燃性ガスとその発生に伴う燃焼エネルギーの減少によって直ちに鎮火することができるため、ポリマー電解質二次電池の安全性をより向上することができる。

【0050】本発明に係る非水電解液電池によれば、正極と、負極と、非水電解液と、前記正極と前記負極とを絶縁し、かつ前記電解液を保持する機能を有するセパレータとを具備し、前記正極、前記負極及び前記セパレータのうち少なくとも一つは、高温において揮発性の不燃性物質を生成する難燃剤を含む。このような電池は、例えば過充電や、高温雰囲気中に晒された際、前記難燃剤が揮発性の不燃性物質を生成し、この不燃性物質が不燃性ガスを発生するため、電池内の温度を低下させることができる。その結果、非水電解液が発火するのを未然に防ぐこ

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とができ、仮に非水電解液が既に燃焼していたとしても前記不燃性ガスとその発生に伴う燃焼エネルギーの減少によって直ちに鎮火することができるため、非水溶媒電池の安全性をより向上することができる。

【0051】また、前記ポリマー電解質二次電池及び前記非水溶媒電池において、前記燃焼剤としてテトラブロモビスフェノールAを用いることによって、過充電や高温雰囲気になされた際に前記テトラブロモビスフェノールAが熱分解し、非水電解液の燃焼により生成したメタンと反応して揮発性が高いHBrが生成する。このHBrは揮発し、不燃性ガスを発生させると共に、このガス発生により燃焼エネルギーが消費されるため、電池内の温度が低下する。その結果、非水電解液の燃焼を直ちに停止することができる。また、この燃焼剤を含むポリマー電解質二次電池は、リチウムイオンの吸蔵・放出反応を阻害しないため、実用的な放電容量及びサイクル寿命を確保することができる。

【0052】また、前記ポリマー電解質二次電池及び前記非水溶媒電池において、前記燃焼剤としてテトラブロモビスフェノールA及び酸化アンチモンからなるものを用いることによって、過充電や高温雰囲気にさらされた際に両者が反応して揮発性が高いSbBr₃や、SbOBrを生成する。これら生成物が揮発することにより電池内の熱が奪われ、電池温度を低下させることができる。また、前記生成物の揮発によって不燃性ガスを発生することができる。その結果、非水電解液の発火を未然に防止することができ、既に非水電解液が燃焼していたとしても前記不燃性ガスの発生によって直ちに鎮火することができる。また、この燃焼剤を含むポリマー電解質二次電池は、リチウムイオンの吸蔵・放出反応を阻害しないため、実用的な放電容量及びサイクル寿命を確保することができる。

【0053】

【実施例】以下、本発明の実施例を前述した図面を参照して詳細に説明する。

<実施例1>

(非水電解液未含浸の正極層の作製) 炭酸リチウム(Li₂CO₃)と二酸化マンガン(MnO₂)をLiとMnのモル比が1:2となるように混合し、この混合物を800℃で24時間焼成することにより組成式がLiMn₂O₄で表されるリチウムマンガン複合酸化物を作製した。

【0054】ビニリデンフロライド-ヘキサフルオロプロピレン(VdF-HFP)の共重合体(VdF:HFPの共重合比は80:20%である)粉末をアセトンに11重量%溶解させてアセトン溶液を調製した後、このアセトン溶液に前記リチウムマンガン複合酸化物が72重量%、導電性材料としてのアセチレンブラックが8重量%を前記共重合体の個形分が20重量%になるように添加し、混合した。更にSb₂O₃粉末とテトラプロモ

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ビスフェノールA粉末を前記共重合体に対してそれぞれ10重量%になるように添加し、混合した。得られた懸濁液をキャストリングにより成膜し、常温にて放置して自然乾燥させることにより電解液未含浸で、厚さが100μmのシート状正極層を作製した。

【0055】(非水電解液未含浸の負極層の作製) ビニリデンフロライド-ヘキサフルオロプロピレン(VdF-HFP)の共重合体(VdF:HFPの共重合比は80:20%である)粉末をアセトンに11重量%溶解させてアセトン溶液を調製した後、このアセトン溶液に活物質として石油コークス(株式会社ベトカ社製、商品名がメルブロンミルド)80重量%を前記共重合体の個形分が20重量%になるように添加し、混合した。更にSb₂O₃粉末とテトラプロモビスフェノールA粉末を前記共重合体に対してそれぞれ10重量%になるように添加し、混合した。得られた懸濁液をキャストリングにより成膜し、常温にて放置して自然乾燥させることにより電解液未含浸で、厚さが100μmのシート状負極層を作製した。

【0056】(電解液未含浸のポリマー電解質フィルムの作製) ビニリデンフロライド-ヘキサフルオロプロピレン(VdF-HFP)の共重合体(VdF:HFPの共重合比は80:20%である)粉末をアセトンに11重量%溶解させてアセトン溶液を調製した。更にSb₂O₃粉末とテトラプロモビスフェノールA粉末を前記共重合体に対してそれぞれ10重量%になるように添加し、混合した。この溶液をキャストリングにより成膜し、常温において乾燥することによって、厚さが30μmのポリマー電解質層を作製した。

【0057】(非水電解液の調製) エチレンカーボネート(EC)とジメチルカーボネート(DMC)が体積比で2:1の割合で混合された非水溶媒に電解質としてのLiPF₆をその濃度が1mol/lになるように溶解させて非水電解液を調製した。

【0058】得られたシート状正極層を正極集電体としてのアルミニウム箔にダブルロールラミネータによって積層し、電解液未含浸のシート状正極を作製した。また、得られたシート状負極層を負極集電体としての銅箔にダブルロールラミネータによって積層し、電解液未含浸のシート状負極を作製した。この正極と負極の間に電解液未含浸のポリマー電解質層を介在させ、ダブルロールラミネータによって接合した。得られた5層積層物を前記非水電解液中に10分間浸漬することにより前述した図1に示すように積層したポリマー電解質二次電池を製造した。

<比較例1>正極層、負極層及び電解質層の作製時にSb₂O₃粉末とテトラプロモビスフェノールA粉末を添加しないこと以外は、実施例1と同様にしてポリマー電解質二次電池を製造した。

【0059】得られた実施例1及び比較例1の二次電池

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について、40 mAの電流で10時間かけて4.2 Vまで充電した後、40 mAの電流で2.7 Vまで放電する充放電を繰り返して、1サイクル目及び50サイクル目の放電容量を測定し、その結果を下記表1に示す。

【0060】また、実施例1及び比較例1の二次電池について、各電池につき50個ずつ用意し、これらを40 mAの電流で10時間かけて4.2 Vまで充電した後、着火試験を行い、延焼の程度を確認した。その結果を下記表2に示す。

【0061】

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	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例1	0	1	49
比較例1	5	17	28

【0063】表1から明らかなように、本実施例1の二次電池は、比較例1の二次電池に比べてほぼ同様な放電容量及びサイクル時の容量維持率を有しており、難燃剤である SiO_2 とテトラプロモビスフェノールAにより放電特性が損なわれないことがわかる。

【0064】一方、表2から明らかなように、本実施例1の二次電池は、着火の際に燃焼を直ちに停止することができ、比較例1の二次電池に比べて難燃性であることがわかる。

<実施例2>以下に説明する電解液未含浸の正極層、電解液未含浸の負極層及び電解液未含浸のポリマー電解質層を用いること以外は、実施例1と同様にしてポリマー電解質二次電池を製造した。

【0065】(非水電解液未含浸の正極層の作製) 実施例1と同様なVdF-HFPの共重合体粉末をアセトンに11重量%溶解させてアセトン溶液を調製した後、このアセトン溶液に実施例1と同様なリチウムマンガン複合酸化物が72重量%、導電性材料としてのアセチレンブラックが8重量%を前記共重合体の固形分が20重量%になるように添加し、混合した。更にテトラプロモビスフェノールA粉末を前記共重合体に対して10重量%になるように添加し、混合した。得られた懸濁液から実施例1と同様にして電解液未含浸で、厚さが100 μm のシート状正極層を作製した。

【0066】(非水電解液未含浸の負極層の作製) 実施例1と同様なVdF-HFPの共重合体粉末をアセトンに11重量%溶解させてアセトン溶液を調製した後、このアセトン溶液に実施例1と同様な石油コークス80重量%を前記共重合体の固形分が20重量%になるように添加し、混合した。更に、テトラプロモビスフェノールA粉末を前記共重合体に対して10重量%になるように添加し、混合した。得られた懸濁液から実施例1と同様

*【表1】

	放電容量 (mAh)	
	1サイクル目	50サイクル目
実施例1	205	183
比較例1	203	184

【0062】

【表2】

にして電解液未含浸で、厚さが100 μm のシート状負極層を作製した。

【0067】(電解液未含浸のポリマー電解質フィルム) 実施例1と同様なVdF-HFPの共重合体粉末をアセトンに11重量%溶解させてアセトン溶液を調製した。更に、テトラプロモビスフェノールA粉末を前記共重合体に対して10重量%になるように添加し、混合した。この溶液から実施例1と同様にして電解液未含浸で、厚さが30 μm のポリマー電解質層を作製した。

<比較例2>正極層、負極層及び電解質層の作製時にテトラプロモビスフェノールA粉末を添加しないこと以外は、実施例2と同様にしてポリマー電解質二次電池を製造した。

【0068】得られた実施例2及び比較例2の二次電池について、前述したのと同様な条件で充放電を行った際の1サイクル目及び50サイクル目の放電容量を測定し、その結果を下記表3に示す。

【0069】また、実施例2及び比較例2の二次電池について、各電池につき50個ずつ用意し、これらを40 mAの電流で10時間かけて4.2 Vまで充電した後、着火試験を行い、延焼の程度を確認した。その結果を下記表4に示す。

【0070】

40 【表3】

	放電容量 (mAh)	
	1サイクル目	50サイクル目
実施例2	203	183
比較例2	204	185

【0071】

【表4】

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	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例2	3	5	42
比較例2	8	20	22

【0072】表3から明らかなように、難燃剤としてテトラブロモビスフェノールAを含む正極、負極及び電解質層を備えた本実施例2の二次電池は、比較例2の二次電池とはほぼ同等な放電容量及びサイクル時の容量維持率を有しており、実用的な放電特性を維持できることがわかる。

【0073】一方、表2から明らかなように、本実施例2の二次電池は、着火の際に燃焼を直ちに停止することができ、比較例2の二次電池に比べて難燃性であることがわかる。

【0074】なお、前述した実施例においては、ポリマー電解質二次電池に適用した例を説明したが、リチウム一次電池や、リチウム二次電池のような非水溶媒を電解液として用いる電池であればどのような電池にも適用す*20

*ることができる。

【0075】

【発明の効果】以上詳述したように、本発明によれば、過充電や、高温雰囲気中に晒されることによる非水電解液の燃焼を未然に回避、もしくは直ちに鎮火することができ、安全性が向上された非水溶媒電池及びポリマー電解質二次電池を提供することができる。

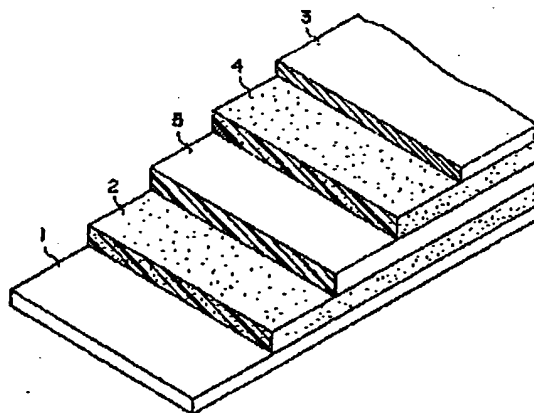
【図面の簡単な説明】

【図1】本発明に係る非水溶媒電池の一例であるポリマー電解質二次電池の積層構造を示す斜視図。

【符号の説明】

1…集電体、2…正極層、4…負極層、5…ポリマー電解質層。

【図1】



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CLAIMS

[Claim(s)]

[Claim 1] It is the non-aqueous-solvent cell which possesses the separator which has the function to insulate the aforementioned positive electrode and the aforementioned negative electrode with a positive electrode, a negative electrode, and nonaqueous electrolyte, and to hold the aforementioned electrolytic solution, and is characterized by at least one containing the flame retarder which generates an volatile noncombustible in an elevated temperature among the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned separator.

[Claim 2] It is the polymer electrolyte rechargeable battery which possesses the solid-state polymer electrolyte layer characterized by providing the following, and is characterized by at least one containing the flame retarder which generates an volatile noncombustible in an elevated temperature among the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned solid-state polymer electrolyte layer. The positive electrode containing the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution. The negative electrode containing the polymer which holds occlusion, the active material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion. Polymer which is arranged between the aforementioned positive electrode and the aforementioned negative electrode, and holds nonaqueous electrolyte and this electrolytic solution.

[Claim 3] The aforementioned flame retarder is a polymer electrolyte rechargeable battery according to claim 2 which consists of tetrabromobisphenol A or is characterized by the bird clapper from tetrabromobisphenol A and an antimony oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a non-aqueous-solvent cell and a polymer electrolyte rechargeable battery equipped with nonaqueous electrolyte.

[0002]

[Description of the Prior Art] In recent years, with development of electronic equipment, it is small, lightweight and an energy density are high, and development of the rechargeable battery in which repeat charge and discharge are still more possible is demanded. The lithium secondary battery possessing the positive electrode which makes an active material oxides, such as a negative electrode which makes a lithium or a lithium alloy an active material, molybdenum and vanadium, titanium, or niobium, a sulfide, or a selenium compound as such a rechargeable battery is known.

[0003] However, since the dendrite of a lithium will occur in a negative electrode if a charge-and-discharge cycle is repeated, the rechargeable battery equipped with the negative electrode which makes a lithium or a lithium alloy an active material has the trouble that a charge-and-discharge cycle life is short.

[0004] Since it is such, the lithium secondary battery which used occlusion and the carbonaceous material to emit is proposed by the negative electrode in a lithium ion like corks, a graphite, a carbon fiber, a resin baking object, and pyrolysis gaseous-phase carbon. Since the aforementioned rechargeable lithium-ion battery can improve degradation of the negative-electrode property by dendrite deposit, it can improve a battery life and safety.

[0005] The lithium intercalation cell which has the high Brit polyelectrolyte by which flexibility was given to the U.S. patent official report No. 5,296,318 by adding polymer at a positive electrode, a negative electrode, and an electrolyte layer as a polymer electrolyte rechargeable battery which is an example of a rechargeable lithium-ion battery and in which a recharge is possible is indicated. The positive electrode of the structure where the positive-electrode layer in which this polymer electrolyte rechargeable battery contains the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector, The negative electrode of the structure where the negative-electrode layer containing the polymer which holds occlusion, the carbonaceous material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion was supported by the charge collector, It has a solid-state polymer electrolyte layer containing the polymer which intervenes between the aforementioned positive-electrode layer and the aforementioned negative-electrode layer, and holds nonaqueous electrolyte and this electrolytic solution. As the aforementioned nonaqueous electrolyte, what dissolved lithium salt in the non-aqueous solvent is used. An inflammable organic solvent is usually used for this non-aqueous solvent. therefore, the aforementioned rechargeable battery -- a surcharge -- or since there is a possibility that the aforementioned non-aqueous solvent may ignite when the temperature in a cell rises by fire existing in near etc. and it becomes an unusual elevated temperature, reservation of the safety to this serves as an important technical problem

[0006] By the way, as polymer holding the nonaqueous electrolyte contained in the aforementioned

positive electrode, the aforementioned negative electrode, and the aforementioned solid-state polymer electrolyte layer, respectively, the copolymer of fluoride vinylidene (VdF)-hexafluoropropylene (HFP) is used conventionally. In this copolymer, VdF contributes to improvement in mechanical strength in the skeleton section of a copolymer, and holds nonaqueous electrolyte. HFP is incorporated in the state amorphous to a copolymer, and functions as the transparency section of a lithium ion, and contributes to maintenance of the nonaqueous electrolyte in VdF. Since a halogen is included, this VdF-HFP copolymer has self-extinguishing. For example, although flame will burn and move and a film will burn if the origin of a fire is brought close to this after processing a VdF-HFP copolymer in the shape of a film, if the origin of a fire is kept away from a film, combustion of a film will stop. However, improvement in the further safety is demanded in such a polymer electrolyte rechargeable battery.

[0007]

[Problem(s) to be Solved by the Invention] The risk of the combustion at the time of the temperature in a cell becoming an unusual elevated temperature by the surcharge etc. is avoided, and the purpose of this invention tends to offer the non-aqueous-solvent cell and polymer electrolyte rechargeable battery whose safety improved.

[0008]

[Means for Solving the Problem] The separator which has the function for the non-aqueous-solvent cell concerning this invention to insulate the aforementioned positive electrode and the aforementioned negative electrode with a positive electrode, a negative electrode, and nonaqueous electrolyte, and to hold the aforementioned electrolytic solution is provided, and at least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned separator is characterized by including the flame retarder which generates an volatile noncombustible in an elevated temperature.

[0009] The positive electrode where the polymer electrolyte rechargeable battery concerning this invention contains the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution, The negative electrode containing the polymer which holds occlusion, the active material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion, The solid-state polymer electrolyte layer containing the polymer which is arranged between the aforementioned positive electrode and the aforementioned negative electrode, and holds nonaqueous electrolyte and this electrolytic solution is provided. At least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned solid-state polymer electrolyte layers is characterized by including the flame retarder which generates an volatile noncombustible in an elevated temperature.

[0010]

[Embodiments of the Invention] Hereafter, the polymer electrolyte rechargeable battery which is an example of the non-aqueous-solvent cell concerning this invention is explained with reference to drawing 1 . That is, a polymer electrolyte rechargeable battery is equipped with the unit cell of a laminated structure as shown in drawing 1 . A positive electrode has the structure which carried out the laminating of the positive-electrode layer 2 to the charge collector 1. A negative electrode has the structure which carried out the laminating of the negative-electrode layer 4 to the charge collector 3, and the aforementioned negative-electrode layer 4 counters the positive-electrode layer 2 of the aforementioned positive electrode, and it is arranged. The solid-state polymer electrolyte layer 5 intervenes between the aforementioned positive-electrode layer 2 and the aforementioned negative-electrode layer 4.

[0011] The polymer electrolyte rechargeable battery concerning this invention can be made into the structure where one of electrolyte layers has been arranged among the positive electrodes A and B mentioned later one of positive electrodes, and among the electrolyte layers A and B later mentioned among one of negative electrodes among the negative electrodes A and B mentioned later. However, the aforementioned rechargeable battery does not become the structure where the electrolyte layer B has been arranged between a positive electrode B and a negative electrode B.

[0012] Hereafter, the aforementioned solid-state polymer electrolyte layer, a positive electrode, and a negative electrode are explained.

(1) As a solid-state polymer electrolyte layer aforementioned solid-state polymer electrolyte layer, the solid-state polymer electrolyte layer A or the solid-state polymer electrolyte layer B explained below is used.

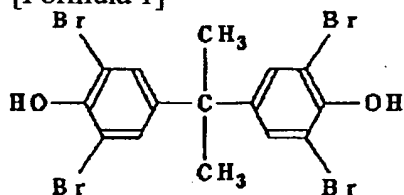
[0013] <Solid-state polymer electrolyte layer A> This solid-state polymer electrolyte layer A contains the flame retarder which generates an volatile noncombustible in nonaqueous electrolyte, the polymer holding this nonaqueous electrolyte, and an elevated temperature.

[0014] The aforementioned flame retarder will generate an volatile noncombustible, if the temperature in the aforementioned rechargeable battery rises [that for example, the aforementioned rechargeable battery is exposed to overcharge and fire atmosphere, etc. and]. When the temperature in the aforementioned cell reaches the ignition point of the non-aqueous solvent contained in the aforementioned nonaqueous electrolyte as the aforementioned flame retarder from a viewpoint which raises the safety of the aforementioned rechargeable battery more, and secures a practical cycle life, it is good in it being what generates an volatile noncombustible.

[0015] What consists of the tetrabromobisphenol A (Tetrabromobisphenol A) which has the structure expression shown in the following-ization 1 as the aforementioned flame retarder, for example or the aforementioned tetrabromobisphenol A, and an antimony oxide (for example, Sb_2O_3) can be used. If the temperature in the aforementioned cell rises at 300-400 degrees C, C-Br combination will dissociate the flame retarder which consists of tetrabromobisphenol A, and it reacts with the methane generated by combustion of nonaqueous electrolyte, and generates a hydrogen bromide (HBr). Since this hydrogen bromide has high volatility, it generates the hydrogen-bromide gas which is noncombustible gas. Moreover, since this generation-of-gas reaction is endothermic reaction, combustion energy decreases. Consequently, since the combustion flame of nonaqueous electrolyte can be intercepted by this noncombustible gas, combustion of a rechargeable battery can be stopped immediately. On the other hand, they are tetrabromobisphenol A and Sb_2O_3 . The flame retarder which consists of an antimony oxide [like] is SbBr_3 when the temperature in the aforementioned cell rises to 400 degrees C. SbOBr is generated. These products are SbBr_3 which is noncombustible gas since volatility is high. Gas and SbOBr gas can be generated and the temperature in a cell can be reduced with volatilization heat. Consequently, it becomes possible to make combustion of nonaqueous electrolyte extinguish immediately, and to prevent combustion of nonaqueous electrolyte.

[0016]

[Formula 1]



[0017] As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a solid-state polymer electrolyte layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0018] As polymer holding the aforementioned nonaqueous electrolyte, the copolymer of the polymer and vinylidene fluoride (VdF) containing a polyethylene-oxide derivative, a polypropylene oxide derivative, and the aforementioned derivative, and hexafluoropropylene (HFP) etc. can be used, for example. In the aforementioned VdF-HFP copolymer, the copolymerization rate of Above HFP is usually just over or below 20 % of the weight at the maximum, although it is dependent also on the

synthetic method of the aforementioned copolymer.

[0019] The aforementioned nonaqueous electrolyte is prepared by dissolving an electrolyte in a non-aqueous solvent. As the aforementioned non-aqueous solvent, ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), gamma-butyrolactone (gamma-BL), a sulfolane, an acetonitrile, 1, 2-dimethoxyethane, 1, 3-dimethoxypropane, a wood ether, a tetrahydrofuran (THF), 2-methyl tetrahydrofuran, etc. can be mentioned. Even if it uses it independently, two or more sorts may use the aforementioned non-aqueous solvent, mixing.

[0020] As the aforementioned electrolyte, the lithium salt of a lithium perchlorate (LiClO_4), a 6 fluoride [phosphoric-acid] lithium (LiPF_6), hexafluorophosphate lithium (LiBF_4), a 6 fluoride arsenic lithium (LiAsF_6), a trifluoromethane sulfonic-acid lithium (LiCF_3SO_3), a screw trifluoromethylsulfonyl imide lithium [$\text{LiN}(\text{CF}_3\text{SO}_3)_2$], etc. can be mentioned, for example.

[0021] As for the amount of dissolutions to the aforementioned non-aqueous solvent of the aforementioned electrolyte, it is desirable to consider as 0.2 mol/l - 2 mol/l. The aforementioned solid electrolyte layer is producible by the method of (1) explained below.

[0022] (1) Prepare the solution of the polymer holding nonaqueous electrolyte, add the aforementioned flame retarder in this solution, form this and dry. Then, nonaqueous electrolyte is infiltrated into this layer and a polymer electrolyte layer is produced.

[0023] <Solid-state polymer electrolyte layer B> This solid-state polymer electrolyte layer B contains the polymer holding nonaqueous electrolyte and this nonaqueous electrolyte.

[0024] The polymer electrolyte layer A mentioned above having explained as the aforementioned nonaqueous electrolyte and polymer and the same thing can be used. After the aforementioned solid electrolyte layer B prepares the solution of the polymer holding nonaqueous electrolyte, forms this and dries, it is producible by infiltrating nonaqueous electrolyte into this layer.

[0025] (2) As the positive-electrode aforementioned positive electrode, the positive electrode A or positive electrode B explained below can be used.

The <positive-electrode A> aforementioned positive electrode A has the structure where the positive-electrode layer containing the polymer holding an active material, the flame retarder which generates an volatile noncombustible in an elevated temperature, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0026] The polymer electrolyte layer mentioned above having explained as the aforementioned flame retarder and the same thing can be used. As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a positive-electrode layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0027] As the aforementioned active material, various oxides (for example, amorphous vanadium pentoxide containing the lithium content cobalt oxide of the lithium content nickel oxide 2 of the lithium manganese multiple oxide of LiMn_2O_4 etc. and manganese dioxide 2, for example, LiNiO etc., for example, LiCoO etc., a lithium content nickel cobalt oxide, and a lithium etc.), chalcogen compounds, etc. (for example, 2 titanium sulfides, 2 sulfuration molybdenum, etc.) can be mentioned. Especially, it is desirable to use a lithium manganese multiple oxide, a lithium content cobalt oxide, and a lithium content nickel oxide.

[0028] The polymer electrolyte layer mentioned above as polymer holding the aforementioned nonaqueous electrolyte having explained and the same thing can be mentioned. You may add conductive material, such as an artificial graphite, carbon black (for example, acetylene black etc.), and nickel powder, in the aforementioned positive-electrode layer of the aforementioned positive electrode.

[0029] As the aforementioned charge collector, an aluminum foil, an aluminum mesh, the expanded

metal made from aluminum, the punched metal made from aluminum, etc. can be mentioned.

[0030] The aforementioned positive electrode is producible by the method of for example, (1) - (2) explained below.

(1) Mix these and produce a positive-electrode layer by forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder, the aforementioned active material, and the aforementioned electrical conducting material in this solution. This positive-electrode layer and the aforementioned charge collector are pasted up by thermocompression bonding etc. A positive electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned positive-electrode layer.

[0031] (2) Mix these and prepare the paste for positive electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder, the aforementioned active material, and the aforementioned electrical conducting material in the aforementioned solution. It is made to dry after carrying out coating of this paste for positive electrodes to the aforementioned charge collector. Nonaqueous electrolyte is infiltrated into the aforementioned positive-electrode layer, and a positive electrode is produced.

[0032] The <positive-electrode B> aforementioned positive electrode B has the structure where the positive-electrode layer containing the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0033] The positive electrode A mentioned above having explained as the aforementioned active material, nonaqueous electrolyte, polymer, and a charge collector and the same thing are used. The aforementioned positive electrode is producible by the method of for example, (1) - (2) explained below.

[0034] (1) Mix these and produce a positive-electrode layer by forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material and the aforementioned electrical conducting material in this solution. This positive-electrode layer and the aforementioned charge collector are pasted up by thermocompression bonding etc. A positive electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned positive-electrode layer.

[0035] (2) Mix these and prepare the paste for positive electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material and the aforementioned electrical conducting material in the aforementioned solution. It is made to dry after carrying out coating of this paste for positive electrodes to the aforementioned charge collector. Nonaqueous electrolyte is infiltrated into the aforementioned positive-electrode layer, and a positive electrode is produced.

[0036] (3) As the negative-electrode aforementioned negative electrode, the negative electrode A or negative electrode B explained below can be used.

[0037] <Negative electrode A> This negative electrode A has the structure where the negative-electrode layer containing the polymer holding the flame retarder which generates an volatile noncombustible for a lithium ion in occlusion, the active material to emit, and an elevated temperature, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0038] The polymer electrolyte layer mentioned above having explained as the aforementioned flame retarder and the same thing can be used. As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a negative-electrode layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0039] As the aforementioned active material, occlusion and the carbonaceous material to emit can be mentioned for a lithium ion. The carbonaceous material represented by the thing and corks which are

obtained as this carbonaceous material by calcinating organic high molecular compounds (for example, phenol resin, a polyacrylonitrile, a cellulose, etc.), for example, what [is obtained by calcinating a pitch], artificial graphite, and natural graphite, etc. can be mentioned. It is desirable to use the carbonaceous material which calcinates the aforementioned organic high molecular compound under an ordinary pressure or reduced pressure, and is obtained at the temperature of 500 degrees C - 3000 degrees C in inert gas atmosphere, such as argon gas and nitrogen gas, especially.

[0040] The polymer electrolyte layer mentioned above as polymer holding the aforementioned nonaqueous electrolyte having explained and the same thing can be used. You may add fillers, such as conductive material, such as artificial graphite and natural graphite, carbon black, acetylene black, KETCHIEN black, nickel powder, and a polyphenylene derivative, olefin system polymer, and a carbon fiber, in the aforementioned negative-electrode layer of the aforementioned negative electrode.

[0041] As the aforementioned charge collector, copper foil, a copper mesh, a copper expanded metal, copper punched metal, etc. can be mentioned. The aforementioned negative electrode A is producible by the method of for example, (1) - (2) explained below.

[0042] (1) Paste up the aforementioned negative-electrode layer and the aforementioned charge collector by thermocompression bonding etc. after producing a negative-electrode layer by mixing these and forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder and the aforementioned active material in this solution. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0043] (2) Mix these and prepare the paste for negative electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder and the aforementioned active material in this solution. It is made to dry after carrying out coating of this paste for negative electrodes to the aforementioned charge collector. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0044] <Negative electrode B> This negative electrode B has the structure where the negative-electrode layer containing the polymer which holds occlusion, the active material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion was supported by the charge collector.

[0045] The negative electrode A mentioned above having explained as the aforementioned active material, the aforementioned electrolytic solution, the aforementioned polymer, and the aforementioned charge collector and the same thing can be mentioned. The aforementioned negative electrode B is producible by the method of for example, (1) - (2) explained below.

[0046] (1) Paste up the aforementioned negative-electrode layer and the aforementioned charge collector by thermocompression bonding etc. after producing a negative-electrode layer by mixing these and forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material in this solution. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0047] (2) Mix these and prepare the paste for negative electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material in this solution. It is made to dry after carrying out coating of this paste for negative electrodes to the aforementioned charge collector. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0048] In addition, you may perform sinking [of the electrolytic solution to electrolytic-solution a non-sunk in positive electrode, a non-sunk in electrolytic-solution electrolyte layer, and electrolytic-solution a non-sunk in negative electrode] in collectively for the laminated structure shown in drawing 1 mentioned above.

[0049] The polymer electrolyte rechargeable battery concerning this invention explained above contains the flame retarder to which any one member generates an volatile noncombustible in an elevated temperature among a positive electrode, a negative electrode, and a solid-state polymer electrolyte layer. If the temperature in a cell rises by exposing such a rechargeable battery to a surcharge and elevated-temperature atmosphere, the aforementioned flame retarder will generate an volatile noncombustible.

This noncombustible volatilizes and generates noncombustible gas. Since this generation-of-gas reaction is endothermic reaction, it can reduce the temperature in a cell. Consequently, since it can be immediately extinguished by reduction of the combustion energy accompanying [though it could prevent that nonaqueous electrolyte ignited and nonaqueous electrolyte has already burned it] the aforementioned noncombustible gas and its generating, the safety of a polymer electrolyte rechargeable battery can be improved more.

[0050] According to the non-aqueous-solvent cell concerning this invention, the separator which has the function to insulate the aforementioned positive electrode and the aforementioned negative electrode with a positive electrode, a negative electrode, and nonaqueous electrolyte, and to hold the aforementioned electrolytic solution is provided, and at least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned separator contains the flame retarder which generates an volatile noncombustible in an elevated temperature. Since the aforementioned flame retarder generates an volatile noncombustible and this noncombustible generates noncombustible gas when exposed to a surcharge and elevated-temperature atmosphere, such a cell can reduce the temperature in a cell. Consequently, since it can be immediately extinguished by reduction of the combustion energy accompanying [though it could prevent that nonaqueous electrolyte ignited and nonaqueous electrolyte has already burned it] the aforementioned noncombustible gas and its generating, the safety of a non-aqueous-solvent cell can be improved more.

[0051] Moreover, in the aforementioned polymer electrolyte rechargeable battery and the aforementioned non-aqueous-solvent cell, by using tetrabromobisphenol A as the aforementioned flame retarder, when exposed to a surcharge or elevated-temperature atmosphere, the aforementioned tetrabromobisphenol A pyrolyzes, and it reacts with the methane generated by combustion of nonaqueous electrolyte, and HBr with high volatility generates. Since combustion energy is consumed by this generation of gas while this HBr volatilizes and generating noncombustible gas, the temperature in a cell falls. Consequently, combustion of nonaqueous electrolyte can be stopped immediately. Moreover, since the polymer electrolyte rechargeable battery containing this flame retarder does not check the occlusion and release reaction of a lithium ion, it can secure practical service capacity and a practical cycle life.

[0052] Moreover, by using what consists of tetrabromobisphenol A and an antimony oxide as the aforementioned flame retarder in the aforementioned polymer electrolyte rechargeable battery and the aforementioned non-aqueous-solvent cell, when exposed to a surcharge or elevated-temperature atmosphere, both react, and it is SbBr_3 with high volatility. SbOBr is generated. When these products volatilize, the heat in a cell is taken and cell temperature can be reduced. Moreover, noncombustible gas can be generated by volatilization of the aforementioned product. Consequently, ignition of nonaqueous electrolyte can be prevented beforehand, and though nonaqueous electrolyte has already burned, it can be immediately extinguished by generating of the aforementioned noncombustible gas. Moreover, since the polymer electrolyte rechargeable battery containing this flame retarder does not check the occlusion and release reaction of a lithium ion, it can secure practical service capacity and a practical cycle life.

[0053]

[Example] Hereafter, with reference to the drawing which mentioned the example of this invention above, it explains in detail.

An empirical formula is LiMn_2O_4 by mixing a <example 1> (production of non-sunk in nonaqueous electrolyte positive-electrode layer) lithium carbonate (Li_2CO_3), and manganese dioxide (MnO_2) so that the mole ratio of Li and Mn may be set to 1:2, and calcinating this mixture at 800 degrees C for 24 hours. The lithium manganese multiple oxide expressed was produced.

[0054] It added so that the acetylene black as a conductive material might become [the aforementioned lithium manganese multiple oxide] this acetone solution 72% of the weight after dissolving the copolymer (copolymerization ratio of VdF:HFP is 80:20%) powder of vinylidene fluoride-hexafluoropropylene (VdF-HFP) in an acetone 11% of the weight and preparing an acetone solution, and the solid content of the aforementioned copolymer might become 20% of the weight about 8 % of the weight, and it mixed. Furthermore, Sb_2O_3 Powder and tetrabromobisphenol A powder were added

[Table 1]

	放電容量 (m A h)	
	1 サイクル目	50 サイクル目
実施例 1	205	183
比較例 1	203	184

[0062]

[Table 2]

	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例 1	0	1	49
比較例 1	5	17	28

[0063] It is Sb 2O₃ which it has the almost same service capacity and the capacity maintenance factor at the time of a cycle even if it compares the rechargeable battery of this example 1 with the rechargeable battery of the example 1 of comparison so that clearly from Table 1, and is a flame retarder. It turns out that an electric discharge property is not spoiled by tetrabromobisphenol A.

[0064] On the other hand, the rechargeable battery of this example 1 can stop combustion immediately in the case of ignition, and it turns out that it is fire retardancy compared with the rechargeable battery of the example 1 of comparison so that clearly from Table 2.

The polymer electrolyte rechargeable battery was manufactured like the example 1 except using the non-sunk in electrolytic-solution positive-electrode layer explained below to <the example 2>, a non-sunk in electrolytic-solution negative-electrode layer, and a non-sunk in electrolytic-solution polymer electrolyte layer.

[0065] (Production of a non-sunk in nonaqueous electrolyte positive-electrode layer) After dissolving the copolymer powder of the same VdF-HFP as an example 1 in the acetone 11% of the weight and preparing an acetone solution, 72% of the weight, the solid content of the aforementioned copolymer added 8 % of the weight so that it might become 20% of the weight, and the acetylene black as a conductive material was mixed by the lithium manganese multiple oxide same in this acetone solution as an example 1. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The sheet-like positive-electrode layer whose thickness is 100 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from the obtained suspension.

[0066] (Production of a non-sunk in nonaqueous electrolyte negative-electrode layer) After dissolving the copolymer powder of the same VdF-HFP as an example 1 in the acetone 11% of the weight and preparing an acetone solution, 80 % of the weight of the petroleum coke same in this acetone solution as an example 1 was added so that the solid content of the aforementioned copolymer might become 20% of the weight, and it mixed. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The sheet-like negative-electrode layer whose thickness is 100 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from the obtained suspension.

[0067] (Production of a non-sunk in electrolytic-solution polymer electrolyte film) The copolymer powder of the same VdF-HFP as an example 1 was dissolved in the acetone 11% of the weight, and the acetone solution was prepared. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The polymer electrolyte layer whose thickness is 30 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from this solution.

The polymer electrolyte rechargeable battery was manufactured like the example 2 except not adding

tetrabromobisphenol A powder at the time of production of the <example 2 of comparison> positive-electrode layer, a negative-electrode layer, and an electrolyte layer.

[0068] About the rechargeable battery of the acquired example 2 and the example 2 of comparison, the service capacity of 1 cycle eye at the time of performing charge and discharge on the conditions same with having mentioned above and 50 cycle eye is measured, and the result is shown in the following table 3.

[0069] Moreover, after preparing every 50 per each cell and charging these to 4.2V over 10 hours about the rechargeable battery of an example 2 and the example 2 of comparison with 40mA current, the ignition examination was performed and the grade of the spread of a fire was checked. The result is shown in the following table 4.

[0070]

[Table 3]

	放電容量 (m A h)	
	1 サイクル目	50 サイクル目
実施例 2	203	183
比較例 2	204	185

[0071]

[Table 4]

	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例 2	3	5	42
比較例 2	8	20	22

[0072] It turns out that the rechargeable battery of this example 2 equipped with the positive electrode, negative electrode, and electrolyte layer which contain tetrabromobisphenol A as a flame retarder has service capacity almost equivalent to the rechargeable battery of the example 2 of comparison, and the capacity maintenance factor at the time of a cycle, and a practical electric discharge property can be maintained so that clearly from Table 3.

[0073] On the other hand, the rechargeable battery of this example 2 can stop combustion immediately in the case of ignition, and it turns out that it is fire retardancy compared with the rechargeable battery of the example 2 of comparison so that clearly from Table 2.

[0074] In addition, in the example mentioned above, although the example applied to the polymer electrolyte rechargeable battery was explained, if it is a lithium primary cell and a cell using a non-aqueous solvent like a lithium secondary battery as the electrolytic solution, it is applicable to any cells.

[0075]

[Effect of the Invention] As explained in full detail above, according to this invention, evasion or the non-aqueous-solvent cell whose safety could be extinguished immediately and improved, and a polymer electrolyte rechargeable battery can be beforehand offered for combustion of a surcharge and the nonaqueous electrolyte by being exposed to elevated-temperature atmosphere.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a non-aqueous-solvent cell and a polymer electrolyte rechargeable battery equipped with nonaqueous electrolyte.

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PRIOR ART

[Description of the Prior Art] In recent years, with development of electronic equipment, it is small, lightweight and an energy density are high, and development of the rechargeable battery in which repeat charge and discharge are still more possible is demanded. The lithium secondary battery possessing the positive electrode which makes an active material oxides, such as a negative electrode which makes a lithium or a lithium alloy an active material, molybdenum and vanadium, titanium, or niobium, a sulfide, or a selenium compound as such a rechargeable battery is known.

[0003] However, since the dendrite of a lithium will occur in a negative electrode if a charge-and-discharge cycle is repeated, the rechargeable battery equipped with the negative electrode which makes a lithium or a lithium alloy an active material has the trouble that a charge-and-discharge cycle life is short.

[0004] Since it is such, the lithium secondary battery which used occlusion and the carbonaceous material to emit is proposed by the negative electrode in a lithium ion like corks, a graphite, a carbon fiber, a resin baking object, and pyrolysis gaseous-phase carbon. Since the aforementioned rechargeable lithium-ion battery can improve degradation of the negative-electrode property by dendrite deposit, it can improve a battery life and safety.

[0005] The lithium intercalation cell which has the high Brit polyelectrolyte by which flexibility was given to the U.S. patent official report No. 5,296,318 by adding polymer at a positive electrode, a negative electrode, and an electrolyte layer as a polymer electrolyte rechargeable battery which is an example of a rechargeable lithium-ion battery and in which a recharge is possible is indicated. This polymer electrolyte rechargeable battery is the positive electrode of the structure where the positive-electrode layer containing the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector. It has a solid-state polymer electrolyte layer containing the polymer which intervenes between the negative electrode of the structure where the negative-electrode layer containing the polymer which holds occlusion, the carbonaceous material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion was supported by the charge collector, and the aforementioned positive-electrode layer and the aforementioned negative-electrode layer, and holds nonaqueous electrolyte and this electrolytic solution. As the aforementioned nonaqueous electrolyte, what dissolved lithium salt in the non-aqueous solvent is used. An inflammable organic solvent is usually used for this non-aqueous solvent. therefore, the aforementioned rechargeable battery -- a surcharge -- or since there is a possibility that the aforementioned non-aqueous solvent may ignite when the temperature in a cell rises by fire existing in near etc. and it becomes an unusual elevated temperature, reservation of the safety to this serves as an important technical problem

[0006] By the way, as polymer holding the nonaqueous electrolyte contained in the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned solid-state polymer electrolyte layer, respectively, the copolymer of fluoride vinylidene (VdF)-hexafluoropropylene (HFP) is used conventionally. In this copolymer, VdF contributes to improvement in mechanical strength in the frame section of a copolymer, and holds nonaqueous electrolyte. HFP is incorporated in the state amorphous to a copolymer, and functions as the transparency section of a lithium ion; and contributes to

maintenance of the nonaqueous electrolyte in VdF. Since a halogen is included, this VdF-HFP copolymer has self-extinguishing. For example, although flame will burn and move and a film will burn if the origin of a fire is brought close to this after processing a VdF-HFP copolymer in the shape of a film, if the origin of a fire is kept away from a film, combustion of a film will stop. However, improvement in the further safety is demanded in such a polymer electrolyte rechargeable battery.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained in full detail above, according to this invention, evasion or the non-aqueous-solvent cell whose safety could be extinguished immediately and improved, and a polymer electrolyte rechargeable battery can be beforehand offered for combustion of a surcharge and the nonaqueous electrolyte by being exposed to elevated-temperature atmosphere.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The risk of the combustion at the time of the temperature in a cell becoming an unusual elevated temperature by the surcharge etc. is avoided, and the purpose of this invention tends to offer the non-aqueous-solvent cell and polymer electrolyte rechargeable battery whose safety improved.

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MEANS

[Means for Solving the Problem] The separator which has the function for the non-aqueous-solvent cell concerning this invention to insulate the aforementioned positive electrode and the aforementioned negative electrode with a positive electrode, a negative electrode, and nonaqueous electrolyte, and to hold the aforementioned electrolytic solution is provided, and at least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned separator is characterized by including the flame retarder which generates an volatile noncombustible in an elevated temperature.

[0009] The positive electrode where the polymer electrolyte rechargeable battery concerning this invention contains the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution, The negative electrode containing the polymer which holds occlusion, the active material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion, The solid-state polymer electrolyte layer containing the polymer which is arranged between the aforementioned positive electrode and the aforementioned negative electrode, and holds nonaqueous electrolyte and this electrolytic solution is provided. At least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned solid-state polymer electrolyte layers is characterized by including the flame retarder which generates an volatile noncombustible in an elevated temperature.

[0010]

[Embodiments of the Invention] Hereafter, the polymer electrolyte rechargeable battery which is an example of the non-aqueous-solvent cell concerning this invention is explained with reference to drawing 1. That is, a polymer electrolyte rechargeable battery is equipped with the unit cell of a laminated structure as shown in drawing 1. A positive electrode has the structure which carried out the laminating of the positive-electrode layer 2 to the charge collector 1. A negative electrode has the structure which carried out the laminating of the negative-electrode layer 4 to the charge collector 3, and the aforementioned negative-electrode layer 4 counters the positive-electrode layer 2 of the aforementioned positive electrode, and it is arranged. The solid-state polymer electrolyte layer 5 intervenes between the aforementioned positive-electrode layer 2 and the aforementioned negative-electrode layer 4.

[0011] The polymer electrolyte rechargeable battery concerning this invention can be made into the structure where one of electrolyte layers has been arranged among the positive electrodes A and B mentioned later one of positive electrodes, and among the electrolyte layers A and B later mentioned among one of negative electrodes among the negative electrodes A and B mentioned later. However, the aforementioned rechargeable battery does not become the structure where the electrolyte layer B has been arranged between a positive electrode B and a negative electrode B.

[0012] Hereafter, the aforementioned solid-state polymer electrolyte layer, a positive electrode, and a negative electrode are explained.

(1) As a solid-state polymer electrolyte layer aforementioned solid-state polymer electrolyte layer, the solid-state polymer electrolyte layer A or the solid-state polymer electrolyte layer B explained below is used.

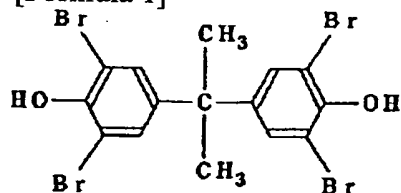
[0013] <Solid-state polymer electrolyte layer A> This solid-state polymer electrolyte layer A contains the flame retarder which generates an volatile noncombustible in nonaqueous electrolyte, the polymer holding this nonaqueous electrolyte, and an elevated temperature.

[0014] The aforementioned flame retarder will generate an volatile noncombustible, if the temperature in the aforementioned rechargeable battery rises [that for example, the aforementioned rechargeable battery is exposed to overcharge and fire atmosphere, etc. and]. When the temperature in the aforementioned cell reaches the ignition point of the non-aqueous solvent contained in the aforementioned nonaqueous electrolyte as the aforementioned flame retarder from a viewpoint which raises the safety of the aforementioned rechargeable battery more, and secures a practical cycle life, it is good in it being what generates an volatile noncombustible.

[0015] What consists of the tetrabromobisphenol A (Tetrabromobisphenol A) which has the structure expression shown in the following-ization 1 as the aforementioned flame retarder, for example or the aforementioned tetrabromobisphenol A, and an antimony oxide (for example, Sb_2O_3) can be used. If the temperature in the aforementioned cell rises at 300-400 degrees C, C-Br combination will dissociate the flame retarder which consists of tetrabromobisphenol A, and it reacts with the methane generated by combustion of nonaqueous electrolyte, and generates a hydrogen bromide (HBr). Since this hydrogen bromide has high volatility, it generates the hydrogen-bromide gas which is noncombustible gas. Moreover, since this generation-of-gas reaction is endothermic reaction, combustion energy decreases. Consequently, since the combustion flame of nonaqueous electrolyte can be intercepted by this noncombustible gas, combustion of a rechargeable battery can be stopped immediately. On the other hand, they are tetrabromobisphenol A and Sb_2O_3 . The flame retarder which consists of an antimony oxide [like] is SbBr_3 when the temperature in the aforementioned cell rises to 400 degrees C. SbOBr is generated. These products are SbBr_3 which is noncombustible gas since volatility is high. Gas and SbOBr gas can be generated and the temperature in a cell can be reduced with volatilization heat. Consequently, it becomes possible to make combustion of nonaqueous electrolyte extinguish immediately, and to prevent combustion of nonaqueous electrolyte.

[0016]

[Formula 1]



[0017] As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a solid-state polymer electrolyte layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0018] As polymer holding the aforementioned nonaqueous electrolyte, the copolymer of the polymer and vinylidene fluoride (VdF) containing a polyethylene-oxide derivative, a polypropylene oxide derivative, and the aforementioned derivative, and hexafluoropropylene (HFP) etc. can be used, for example. In the aforementioned VdF-HFP copolymer, the copolymerization rate of Above HFP is usually just over or below 20 % of the weight at the maximum, although it is dependent also on the synthetic method of the aforementioned copolymer.

[0019] The aforementioned nonaqueous electrolyte is prepared by dissolving an electrolyte in a non-aqueous solvent. As the aforementioned non-aqueous solvent, ethylene carbonate (EC), propylene

carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), gamma-butyrolactone (gamma-BL), a sulfolane, an acetonitrile, 1, 2-dimethoxyethane, 1, 3-dimethoxypropane, a wood ether, a tetrahydrofuran (THF), 2-methyl tetrahydrofuran, etc. can be mentioned. Even if it uses it independently, two or more sorts may use the aforementioned non-aqueous solvent, mixing.

[0020] As the aforementioned electrolyte, the lithium salt of a lithium perchlorate (LiClO_4), a 6 fluoride [phosphoric-acid] lithium (LiPF_6), hexafluorophosphate lithium (LiBF_4), a 6 fluoride arsenic lithium (LiAsF_6), a trifluoromethane sulfonic-acid lithium (LiCF_3SO_3), a screw trifluoromethylsulfonyl imide lithium [$\text{LiN}(\text{CF}_3\text{SO}_3)_2$], etc. can be mentioned, for example.

[0021] As for the amount of dissolutions to the aforementioned non-aqueous solvent of the aforementioned electrolyte, it is desirable to consider as 0.2 mol/l - 2 mol/l. The aforementioned solid electrolyte layer is producible by the method of (1) explained below.

[0022] (1) Prepare the solution of the polymer holding nonaqueous electrolyte, add the aforementioned flame retarder in this solution, form this and dry. Then, nonaqueous electrolyte is infiltrated into this layer and a polymer electrolyte layer is produced.

[0023] <Solid-state polymer electrolyte layer B> This solid-state polymer electrolyte layer B contains the polymer holding nonaqueous electrolyte and this nonaqueous electrolyte.

[0024] The polymer electrolyte layer A mentioned above having explained as the aforementioned nonaqueous electrolyte and polymer and the same thing can be used. After the aforementioned solid electrolyte layer B prepares the solution of the polymer holding nonaqueous electrolyte, forms this and dries, it is producible by infiltrating nonaqueous electrolyte into this layer.

[0025] (2) As the positive-electrode aforementioned positive electrode, the positive electrode A or positive electrode B explained below can be used.

The <positive-electrode A> aforementioned positive electrode A has the structure where the positive-electrode layer containing the polymer holding an active material, the flame retarder which generates an volatile noncombustible in an elevated temperature, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0026] The polymer electrolyte layer mentioned above having explained as the aforementioned flame retarder and the same thing can be used. As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a positive-electrode layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0027] As the aforementioned active material, various oxides (for example, amorphous vanadium pentoxide containing the lithium content cobalt oxide of the lithium content nickel oxide 2 of the lithium manganese multiple oxide of LiMn_2O_4 etc. and manganese dioxide 2, for example, LiNiO etc., for example, LiCoO etc., a lithium content nickel cobalt oxide, and a lithium etc.), chalcogen compounds, etc. (for example, 2 titanium sulfides, 2 sulfuration molybdenum, etc.) can be mentioned. Especially, it is desirable to use a lithium manganese multiple oxide, a lithium content cobalt oxide, and a lithium content nickel oxide.

[0028] The polymer electrolyte layer mentioned above as polymer holding the aforementioned nonaqueous electrolyte having explained and the same thing can be mentioned. You may add conductive material, such as an artificial graphite, carbon black (for example, acetylene black etc.), and nickel powder, in the aforementioned positive-electrode layer of the aforementioned positive electrode.

[0029] As the aforementioned charge collector, an aluminum foil, an aluminum mesh, the expanded metal made from aluminum, the punched metal made from aluminum, etc. can be mentioned.

[0030] The aforementioned positive electrode is producible by the method of for example, (1) - (2) explained below.

(1) Mix these and produce a positive-electrode layer by forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder, the aforementioned active material, and the aforementioned electrical conducting material in this solution. This positive-electrode layer and the aforementioned charge collector are pasted up by thermocompression bonding etc. A positive electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned positive-electrode layer.

[0031] (2) Mix these and prepare the paste for positive electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder, the aforementioned active material, and the aforementioned electrical conducting material in the aforementioned solution. It is made to dry after carrying out coating of this paste for positive electrodes to the aforementioned charge collector. Nonaqueous electrolyte is infiltrated into the aforementioned positive-electrode layer, and a positive electrode is produced.

[0032] The <positive-electrode B> aforementioned positive electrode B has the structure where the positive-electrode layer containing the polymer holding an active material, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0033] The positive electrode A mentioned above having explained as the aforementioned active material, nonaqueous electrolyte, polymer, and a charge collector and the same thing are used. The aforementioned positive electrode is producible by the method of for example, (1) - (2) explained below.

[0034] (1) Mix these and produce a positive-electrode layer by forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material and the aforementioned electrical conducting material in this solution. This positive-electrode layer and the aforementioned charge collector are pasted up by thermocompression bonding etc. A positive electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned positive-electrode layer.

[0035] (2) Mix these and prepare the paste for positive electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material and the aforementioned electrical conducting material in the aforementioned solution. It is made to dry after carrying out coating of this paste for positive electrodes to the aforementioned charge collector. Nonaqueous electrolyte is infiltrated into the aforementioned positive-electrode layer, and a positive electrode is produced.

[0036] (3) As the negative-electrode aforementioned negative electrode, the negative electrode A or negative electrode B explained below can be used.

[0037] <Negative electrode A> This negative electrode A has the structure where the negative-electrode layer containing the polymer holding the flame retarder which generates an volatile noncombustible for a lithium ion in occlusion, the active material to emit, and an elevated temperature, nonaqueous electrolyte, and this electrolytic solution was supported by the charge collector.

[0038] The polymer electrolyte layer mentioned above having explained as the aforementioned flame retarder and the same thing can be used. As for the loadings of the aforementioned flame retarder, it is desirable to make it 5 - 20% of the weight of the range to the polymer holding the aforementioned nonaqueous electrolyte. This is based on the following reasons. When the aforementioned loadings are carried out to less than 5% of the weight, there is a possibility that it may become difficult to fully demonstrate a fire-resistant operation. On the other hand, when the aforementioned loadings exceed 20 % of the weight, there is a possibility that the mechanical strength of a negative-electrode layer may fall extremely, and may have a bad influence on configuration maintenance of a cell. More desirable loadings are 8 - 15% of the weight of a range.

[0039] As the aforementioned active material, occlusion and the carbonaceous material to emit can be mentioned for a lithium ion. The carbonaceous material represented by the thing and corks which are obtained as this carbonaceous material by calcinating organic high molecular compounds (for example, phenol resin, a polyacrylonitrile, a cellulose, etc.), for example, what [is obtained by calcinating a pitch], artificial graphite, and natural graphite, etc. can be mentioned. It is desirable to use the

carbonaceous material which calcinates the aforementioned organic high molecular compound under an ordinary pressure or reduced pressure, and is obtained at the temperature of 500 degrees C - 3000 degrees C in inert gas atmosphere, such as argon gas and nitrogen gas, especially.

[0040] The polymer electrolyte layer mentioned above as polymer holding the aforementioned nonaqueous electrolyte having explained and the same thing can be used. You may add fillers, such as conductive material, such as artificial graphite and natural graphite, carbon black, acetylene black, KETCHIEN black, nickel powder, and a polyphenylene derivative, olefin system polymer, and a carbon fiber, in the aforementioned negative-electrode layer of the aforementioned negative electrode.

[0041] As the aforementioned charge collector, copper foil, a copper mesh, a copper expanded metal, copper punched metal, etc. can be mentioned. The aforementioned negative electrode A is producible by the method of for example, (1) - (2) explained below.

[0042] (1) Paste up the aforementioned negative-electrode layer and the aforementioned charge collector by thermocompression bonding etc. after producing a negative-electrode layer by mixing these and forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder and the aforementioned active material in this solution. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0043] (2) Mix these and prepare the paste for negative electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned flame retarder and the aforementioned active material in this solution. It is made to dry after carrying out coating of this paste for negative electrodes to the aforementioned charge collector. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0044] <Negative electrode B> This negative electrode B has the structure where the negative-electrode layer containing the polymer which holds occlusion, the active material to emit, nonaqueous electrolyte, and this electrolytic solution for a lithium ion was supported by the charge collector.

[0045] The negative electrode A mentioned above having explained as the aforementioned active material, the aforementioned electrolytic solution, the aforementioned polymer, and the aforementioned charge collector and the same thing can be mentioned. The aforementioned negative electrode B is producible by the method of for example, (1) - (2) explained below.

[0046] (1) Paste up the aforementioned negative-electrode layer and the aforementioned charge collector by thermocompression bonding etc. after producing a negative-electrode layer by mixing these and forming membranes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material in this solution. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0047] (2) Mix these and prepare the paste for negative electrodes, after preparing the solution of the polymer holding nonaqueous electrolyte and adding the aforementioned active material in this solution. It is made to dry after carrying out coating of this paste for negative electrodes to the aforementioned charge collector. A negative electrode is produced by infiltrating nonaqueous electrolyte into the aforementioned negative-electrode layer.

[0048] In addition, you may perform sinking [of the electrolytic solution to electrolytic-solution a non-sunk in positive electrode, a non-sunk in electrolytic-solution electrolyte layer, and electrolytic-solution a non-sunk in negative electrode] in collectively for the laminated structure shown in drawing 1 mentioned above.

[0049] The polymer electrolyte rechargeable battery concerning this invention explained above contains the flame retarder to which any one member generates an volatile noncombustible in an elevated temperature among a positive electrode, a negative electrode, and a solid-state polymer electrolyte layer. If the temperature in a cell rises by exposing such a rechargeable battery to a surcharge and elevated-temperature atmosphere, the aforementioned flame retarder will generate an volatile noncombustible. This noncombustible volatilizes and generates noncombustible gas. Since this generation-of-gas reaction is endothermic reaction, it can reduce the temperature in a cell. Consequently, since it can be immediately extinguished by reduction of the combustion energy accompanying [though it could

prevent that nonaqueous electrolyte ignited and nonaqueous electrolyte has already burned it] the aforementioned noncombustible gas and its generating, the safety of a polymer electrolyte rechargeable battery can be improved more.

[0050] According to the non-aqueous-solvent cell concerning this invention, the separator which has the function to insulate the aforementioned positive electrode and the aforementioned negative electrode with a positive electrode, a negative electrode, and nonaqueous electrolyte, and to hold the aforementioned electrolytic solution is provided, and at least one of the aforementioned positive electrode, the aforementioned negative electrode, and the aforementioned separator contains the flame retarder which generates an volatile noncombustible in an elevated temperature. Since the aforementioned flame retarder generates an volatile noncombustible and this noncombustible generates noncombustible gas when exposed to a surcharge and elevated-temperature atmosphere, such a cell can reduce the temperature in a cell. Consequently, since it can be immediately extinguished by reduction of the combustion energy accompanying [though it could prevent that nonaqueous electrolyte ignited and nonaqueous electrolyte has already burned it] the aforementioned noncombustible gas and its generating, the safety of a non-aqueous-solvent cell can be improved more.

[0051] Moreover, in the aforementioned polymer electrolyte rechargeable battery and the aforementioned non-aqueous-solvent cell, by using tetrabromobisphenol A as the aforementioned flame retarder, when exposed to a surcharge or elevated-temperature atmosphere, the aforementioned tetrabromobisphenol A pyrolyzes, and it reacts with the methane generated by combustion of nonaqueous electrolyte, and HBr with high volatility generates. Since combustion energy is consumed by this generation of gas while this HBr volatilizes and generating noncombustible gas, the temperature in a cell falls. Consequently, combustion of nonaqueous electrolyte can be stopped immediately. Moreover, since the polymer electrolyte rechargeable battery containing this flame retarder does not check the occlusion and release reaction of a lithium ion, it can secure practical service capacity and a practical cycle life.

[0052] Moreover, by using what consists of tetrabromobisphenol A and an antimony oxide as the aforementioned flame retarder in the aforementioned polymer electrolyte rechargeable battery and the aforementioned non-aqueous-solvent cell, when exposed to a surcharge or elevated-temperature atmosphere, both react, and it is SbBr_3 with high volatility. SbOBr is generated. When these products volatilize, the heat in a cell is taken and cell temperature can be reduced. Moreover, noncombustible gas can be generated by volatilization of the aforementioned product. Consequently, ignition of nonaqueous electrolyte can be prevented beforehand, and though nonaqueous electrolyte has already burned, it can be immediately extinguished by generating of the aforementioned noncombustible gas. Moreover, since the polymer electrolyte rechargeable battery containing this flame retarder does not check the occlusion and release reaction of a lithium ion, it can secure practical service capacity and a practical cycle life.

[Translation done.]

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EXAMPLE

[Example] Hereafter, with reference to the drawing which mentioned the example of this invention above, it explains in detail.

An empirical formula is LiMn_2O_4 by mixing a <example 1> (production of non-sunk in nonaqueous electrolyte positive-electrode layer) lithium carbonate (Li_2CO_3), and manganese dioxide (MnO_2) so that the mole ratio of Li and Mn may be set to 1:2, and calcinating this mixture at 800 degrees C for 24 hours. The lithium manganese multiple oxide expressed was produced.

[0054] It added so that the acetylene black as a conductive material might become [the aforementioned lithium manganese multiple oxide] this acetone solution 72% of the weight after dissolving the copolymer (copolymerization ratio of VdF:HFP is 80:20%) powder of vinylidene fluoride-hexafluoropropylene (VdF-HFP) in an acetone 11% of the weight and preparing an acetone solution, and the solid content of the aforementioned copolymer might become 20% of the weight about 8 % of the weight, and it mixed. Furthermore, Sb_2O_3 Powder and tetrabromobisphenol A powder were added so that it might become 10% of the weight to the aforementioned copolymer, respectively, and it mixed. The obtained suspension was formed by casting and thickness produced the sheet-like positive-electrode layer which is 100 micrometers by electrolytic-solution un-sinking in by leaving and carrying out an air drying in ordinary temperature.

[0055] (Production of a non-sunk in nonaqueous electrolyte negative-electrode layer) After dissolving the copolymer (copolymerization ratio of VdF:HFP is 80:20%) powder of vinylidene fluoride-hexafluoropropylene (VdF-HFP) in the acetone 11% of the weight and preparing an acetone solution, it added so that the solid content of the aforementioned copolymer might become 20% of the weight in this acetone solution as an active material in 80 % of the weight (it is a product made from PETOKA, Inc., and a tradename is mel BUROMMIRUDO) of petroleum coke, and mixed. Furthermore, Sb_2O_3 Powder and tetrabromobisphenol A powder were added so that it might become 10% of the weight to the aforementioned copolymer, respectively, and it mixed. The obtained suspension was formed by casting and thickness produced the sheet-like negative-electrode layer which is 100 micrometers by electrolytic-solution un-sinking in by leaving and carrying out an air drying in ordinary temperature.

[0056] (Production of a non-sunk in electrolytic-solution polymer electrolyte film) The copolymer (copolymerization ratio of VdF:HFP is 80:20%) powder of vinylidene fluoride-hexafluoropropylene (VdF-HFP) was dissolved in the acetone 11% of the weight, and the acetone solution was prepared. Furthermore, Sb_2O_3 Powder and tetrabromobisphenol A powder were added so that it might become 10% of the weight to the aforementioned copolymer, respectively, and it mixed. Thickness produced the polymer electrolyte layer which is 30 micrometers by forming this solution by casting and drying in ordinary temperature.

[0057] (Manufacture of nonaqueous electrolyte) It is LiPF_6 as an electrolyte to the non-aqueous solvent with which ethylene carbonate (EC) and dimethyl carbonate (DMC) were mixed at a rate of 2:1 by the volume ratio. It was made to dissolve so that the concentration may become 1 mol/l, and nonaqueous electrolyte was prepared.

[0058] The laminating of the obtained sheet-like positive-electrode layer was carried out to the

aluminum foil as a positive-electrode charge collector with the double roll laminator, and the non-sunk in electrolytic-solution sheet-like positive electrode was produced. Moreover, the laminating of the obtained sheet-like negative-electrode layer was carried out to the copper foil as a negative-electrode charge collector with the double roll laminator, and the non-sunk in electrolytic-solution sheet-like negative electrode was produced. The non-sunk in electrolytic-solution polymer electrolyte layer was made to intervene between this positive electrode and a negative electrode, and it pasted up with the double roll laminator. The polymer electrolyte rechargeable battery which carried out the laminating as shown in drawing 1 which mentioned above the obtained five-layer laminated material by being immersed for 10 minutes into the aforementioned nonaqueous electrolyte was manufactured.

It is Sb 2O₃ at the time of production of the <example 1 of comparison> positive-electrode layer, a negative-electrode layer, and an electrolyte layer. The polymer electrolyte rechargeable battery was manufactured like the example 1 except not adding powder and tetrabromobisphenol A powder.

[0059] About the rechargeable battery of the acquired example 1 and the example 1 of comparison, after charging to 4.2V over 10 hours with 40mA current, it carries out by repeating the charge and discharge which discharge to 2.7V with 40mA current, the service capacity of 1 cycle eye and 50 cycle eye is measured, and the result is shown in the following table 1.

[0060] Moreover, after preparing every 50 per each cell and charging these to 4.2V over 10 hours about the rechargeable battery of an example 1 and the example 1 of comparison with 40mA current, the ignition examination was performed and the grade of the spread of a fire was checked. The result is shown in the following table 2.

[0061]

[Table 1]

	放電容量 (mA h)	
	1 サイクル目	50 サイクル目
実施例 1	205	183
比較例 1	203	184

[0062]

[Table 2]

	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例 1	0	1	49
比較例 1	5	17	28

[0063] It is Sb 2O₃ which it has the almost same service capacity and the capacity maintenance factor at the time of a cycle even if it compares the rechargeable battery of this example 1 with the rechargeable battery of the example 1 of comparison so that clearly from Table 1, and is a flame retarder. It turns out that an electric discharge property is not spoiled by tetrabromobisphenol A.

[0064] On the other hand, the rechargeable battery of this example 1 can stop combustion immediately in the case of ignition, and it turns out that it is fire retardancy compared with the rechargeable battery of the example 1 of comparison so that clearly from Table 2.

The polymer electrolyte rechargeable battery was manufactured like the example 1 except using the non-sunk in electrolytic-solution positive-electrode layer explained below to <the example 2>, a non-sunk in electrolytic-solution negative-electrode layer, and a non-sunk in electrolytic-solution polymer electrolyte layer.

[0065] (Production of a non-sunk in nonaqueous electrolyte positive-electrode layer) After dissolving the copolymer powder of the same VdF-HFP as an example 1 in the acetone 11% of the weight and

preparing an acetone solution, 72% of the weight, the solid content of the aforementioned copolymer added 8 % of the weight so that it might become 20% of the weight, and the acetylene black as a conductive material was mixed by the lithium manganese multiple oxide same in this acetone solution as an example 1. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The sheet-like positive-electrode layer whose thickness is 100 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from the obtained suspension.

[0066] (Production of a non-sunk in nonaqueous electrolyte negative-electrode layer) After dissolving the copolymer powder of the same VdF-HFP as an example 1 in the acetone 11% of the weight and preparing an acetone solution, 80 % of the weight of the petroleum coke same in this acetone solution as an example 1 was added so that the solid content of the aforementioned copolymer might become 20% of the weight, and it mixed. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The sheet-like negative-electrode layer whose thickness is 100 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from the obtained suspension.

[0067] (Production of a non-sunk in electrolytic-solution polymer electrolyte film) The copolymer powder of the same VdF-HFP as an example 1 was dissolved in the acetone 11% of the weight, and the acetone solution was prepared. Furthermore, tetrabromobisphenol A powder was added so that it might become 10% of the weight to the aforementioned copolymer, and it mixed. The polymer electrolyte layer whose thickness is 30 micrometers was produced by electrolytic-solution un-sinking in as well as an example 1 from this solution.

The polymer electrolyte rechargeable battery was manufactured like the example 2 except not adding tetrabromobisphenol A powder at the time of production of the <example 2 of comparison> positive-electrode layer, a negative-electrode layer, and an electrolyte layer.

[0068] About the rechargeable battery of the acquired example 2 and the example 2 of comparison, the service capacity of 1 cycle eye at the time of performing charge and discharge on the conditions same with having mentioned above and 50 cycle eye is measured, and the result is shown in the following table 3.

[0069] Moreover, after preparing every 50 per each cell and charging these to 4.2V over 10 hours about the rechargeable battery of an example 2 and the example 2 of comparison with 40mA current, the ignition examination was performed and the grade of the spread of a fire was checked. The result is shown in the following table 4.

[0070]

[Table 3]

	放電容量 (m A h)	
	1 サイクル目	50 サイクル目
実施例 2	203	183
比較例 2	204	185

[0071]

[Table 4]

	電池が全焼 (個)	電池が半焼 (個)	直ちに燃焼停止 (個)
実施例 2	3	5	42
比較例 2	8	20	22

[0072] It turns out that the rechargeable battery of this example 2 equipped with the positive electrode,

negative electrode, and electrolyte layer which contain tetrabromobisphenol A as a flame retarder has service capacity almost equivalent to the rechargeable battery of the example 2 of comparison, and the capacity maintenance factor at the time of a cycle, and a practical electric discharge property can be maintained so that clearly from Table 3.

[0073] On the other hand, the rechargeable battery of this example 2 can stop combustion immediately in the case of ignition, and it turns out that it is fire retardancy compared with the rechargeable battery of the example 2 of comparison so that clearly from Table 2.

[0074] In addition, in the example mentioned above, although the example applied to the polymer electrolyte rechargeable battery was explained, if it is a lithium primary cell and a cell using a non-aqueous solvent like a lithium secondary battery as the electrolytic solution, it is applicable to any cells.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The perspective diagram showing the laminated structure of the polymer electrolyte rechargeable battery which is an example of the non-aqueous-solvent cell concerning this invention.

[Description of Notations]

1 3 [-- A negative-electrode layer, 5 / -- Polymer electrolyte layer.] -- A charge collector, 2 -- A positive-electrode layer, 4

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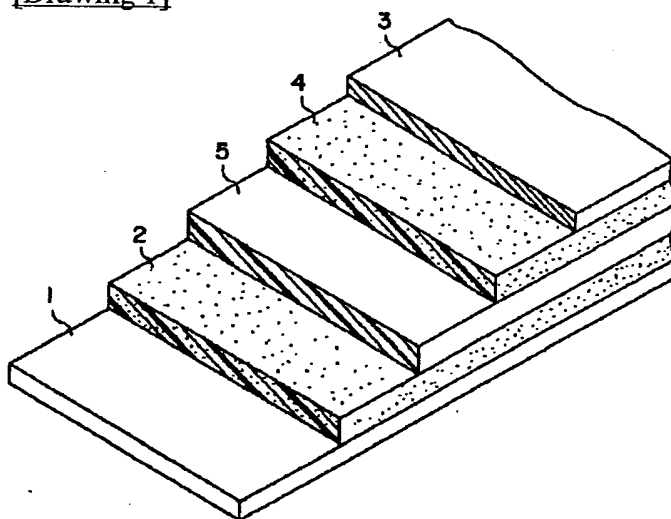
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DRAWINGS

[Drawing 1]



[Translation done.]